POLAROGRAPHY IN LIQUID AMMONIA

BY

CARL JOHN NYMAN, JR.

B. S., The Tulane University of Louisiana, 1944

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

There has been no report of any previous application of polarography to liquid ammonia, even though the electrochemical properties of this solvent have been extensively investigated. It was decided to investigate this branch of electrochemistry in ammonia, since ammonia is remarkably parallel to water in both its solvent and electrochemical properties.

The Ilkovic equation[1] has been found to account for the rate of diffusion of ions to the dropping mercury electrode in water, and it was desired to determine the validity of this equation in liquid ammonia. The values of the ionic diffusion coefficients as evaluated by this equation can be compared with those calculated from an equation derived by Nernst[2] which involves the equivalent ionic conductances of the ions at infinite dilution.

The half-wave potentials can be evaluated theoretically by means of an equation derived with Lingane[3] and by von Stackelberg[4], and these values can be compared with those measured experimentally.

Makishima[5] has postulated that an electrode such as platinum in a solution of metal ions and electrons should function as an electron electrode. He also calculated a theoretical value of —2.45 volts for the standard potential of the electron electrode versus the standard potential of a lead electrode at —34°C. He pointed out that on electrolysis of solutions of salts, several cathodic processes are possible. Reduction of metal ions either to the metal or to a lower valence state are possible reactions. Hydrogen discharge and the transfer of electrons from electrode to the solution are still other processes which might take place. Several investigators have found the latter process to occur on elec-

trolysis of tetraalkyl ammonium salts and metallic salts where the posititve ion is not reduced. The observation was made by Kraus[6] that the electron transfer from electrode to solution was the only cathodic process which occurred on electrolysis of sodium solutions with platinum electrodes. It should be possible to study this process polarographically with a stationary platinum electrode and also with a dropping mercury electrode. In the case of the platinum electrode, the cation of the salt is not important as long as it is one which is normally stable in solution in the presence of electrons. In the case of the dropping mercury electrode, the dissolution of electrons must occur at potentials more positive than that at which positive ions amalgamate. Kraus also found that the only anodic process which occurred at a platinum electrode on electrolysis of sodium solutions was the transfer of electrons from solution to the electrode. It should also be possible to study this process polarographically.

Experimental

A Sargent Model XX Polarograph was used in this investigation and a potentiometer was connected to the circuit so that measurements of the applied potential could be made more accurately than those indicated by the polarograph. The ammonia was dried with sodium metal, and then it was distilled into the electrolysis cell which was so constructed that the mercury pool in the bottom could be used as the reference eelctrode. The system for preparing the solutions was constructed in such a manner that the complete absence of air and water were assured. The dropping mercury electrode was the conventional type used in polarographic studies, and the platinum electrode consisted of a disc sealed at the end of a glass tube. The thermostat used held the temperature at $-36.0 \pm 0.2°C$.

Discussion

The ionic diffusion coefficients of the alkali metals, as

calculated from the Ilkovic equation after measuring the diffusion currents, were found to be slightly higher than those calculated from Nernst's equation. This was attributed to the fact that the migration current was not suppressed completely, because the indifferent electrolyte had a low solubility. It is believed that if higher ratios of indifferent electrolyte to reducible ion were to be used, the Ilkovic equation would be valid.

The half-wave potentials of the alkali metal ions were measured and shown to agree with those calculated theoretically from Lingane's equation. A new equation was derived which gave the same values of the half-wave potentials as those obtained from that derived by Lingane. It was found that the half-wave potentials of the alkali metal ions became more positive as the atomic number increased, and this was attributed to the higher solvation energy of the smaller ions and to the higher free energy of amalgamation of the larger ions. The slopes of the polarograms indicated a reasonable approach to reversibility, but in no case was a theoretical slope observed.

Using a platinum cathode, it was found that the current-voltage curves obtained on electrolysis of solutions of lithium, sodium, tetramethyl ammonium, and tetrabutyl ammonium iodides were almost identical. This indicates that the same process took place with each salt, namely, the transfer of electrons from the electrode to the solution. An anodic current, corresponding to a transfer of electrons from the solution to the electrode, was observed on electrolysis of a solution of sodium metal. As the potential of the electrode was made more negative, the current decreased and became cathodic. The shape of this current-voltage curve was very similar to that observed with the salt solutions.

The dropping mercury electrode showed a behavior very similar to that of platinum. Current-voltage curves, almost identical with those obtained with a platinum electrode on the electrolysis of salt solutions, were obtained with tetra-

propyl ammonium iodide and tetrabutyl ammonium iodide. An entirely different type of curve was obtained with sodium iodide, because the sodium ion forms an amalgam at potentials more positive than that of electron dissolution. It was found that tetrabutyl ammonium ion did not form an amalgam at the surface of the dropping mercury electrode, and therefore the process that occurred must have been the same as with a platinum electrode. On electrolysis of a solution of tetrabutyl ammonium ions and electrons with a dropping mercury electrode, the same type of anodic current-voltage curve was obtained as with the platinum electrode in a sodium solution. It was concluded that in the absence of any reducible ion, the dropping mercury electrode also functions as an electron electrode.

It was found that the hydrogen overvoltage of the metal used as electrode played an important role in determining which electrode process took place. In order for a metal to behave as an electron electrode, the potential of electron dissolution from its surface must be more positive than that of hydrogen discharge.

The standard potential of the electron electrode was estimated to be 2.18 volts more negative than the standard potential of a lead electrode at —36°C.

Summary

1. The Ilkovic equation was found to account for the rate of diffsuion of ions to the surface of the dropping mercury electrode in liquid ammonia, and the diffusion coefficients of the alkali metal ions were measured.

2. The half-wave potentials of the alkali metal ions were found to agree with those calculated theoretically.

3. The platinum and dropping mercury electrodes were found to function as electron electrodes when there were no reducible ions in the solution and when hydrogen discharge did not occur.

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VITA

The author was born in New Orleans, Louisiana, on October 21, 1924. He attended public schools in New Orleans and was graduated from Martin Behrman High School in June, 1940. In September of the same year, he enrolled as a student in the College of Arts and Sciences of Tulane University. During his senior year, he held an undergraduate teaching assistantship in the Department of Chemistry. Following his graduation in February, 1944, with a Bachelor of Science degree, he worked for the Shell Oil Company in Wilmington, California, in the capacity of Junior Technologist. He returned to Tulane University in November of 1944 to continue his studies and was awarded the E. V. Benjamin Research Fellowship. After receiving the degree of Master of Science in Chemistry from Tulane University, he entered the Graduate School of the University of Illinois and held a teaching assistantship in the Inorganic Division of the Department of Chemistry until June, 1947. He was then appointed to a University Fellowship which he has held until the present time.

The author is a member of the American Chemical Society, Sigma Xi, Alpha Chi Sigma, and Phi Lambda Upsilon.